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Mean spherical model and structure of liquid krypton

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Using the mean spherical model (MSM) approximation and square-well potential the Fourier transform of the direct correlation function (DCF) was evaluated and applied in the computation of the structure factor and the radial distribution function of krypton at 210°K. Both the structure factor and radial distribution function show deviations from the experiment while there is close agreement between those derived by Khan from Percus-Yevick (PY) and convolution hypernetted chain (CHNC) equations using Lennard-Jones (LJ) 6–12 and Guggenheim-McGlashan (GM) potentials. From the close agreement of the structure factor and the radial distribution function (RDF) derived from three different potential functions using three different equations (MSM, CHNC, and PY) it is concluded that the experimental values near the critical temperature might be in error and the theoretical RDF is more reliable.

1. Introduction

The mean spherical model (MSM) (Percus & Yevick 1958) which is a perturbation version of Percus-Yevick (PY) theory of hard sphere model is based on the assumption that

$$c(r) = [e(r)-1]y(r), \tag{1}$$

where $c(r)$ is the direct correlation function (DCF), $e(r) = \exp(-u(r)/kT)$ and $y(r) = g(r)/e(r)$ and is valid for all r. However, Lebowitz & Percus (1966) assumed that eq. (1) is valid only for $r < \sigma$, where σ is such that $u(\sigma) = 0$ while for $r < \sigma$ they assumed that

$$c(r) = -u(r)/kT. \tag{2}$$

The square-well potential used in the present calculations can be treated as a perturbation on the hard-core. Just as the perturbation theory (Barker & Henderson 1967) has been found to be a successful theory of fluids it might be possible that the MSM theory would also be useful as a theory of fluids. In fact Blum & Narten (1972) have found the RDF of the MSM to be in excellent agreement with simulation results for a model of liquid sodium. It was also found by Watts *et al* (1972) that the MSM radial distribution function is somewhat better than the PY theory. With these results in view it is felt worthwhile

to investigate the structure factor and the RDF of Krypton at the high temperature where it is hoped that the theoretical evaluation yields better results.

Neutron diffraction measurements of liquid krypton have been made by Clayton & Heaton (1961) over a wide range of temperatures and densities. Khan (1964) made extensive theoretical computations by solving the PY and CHNC equations using Lennard-Jones (LJ) 6–12 and Guggenheim & McGlashan (GM) potentials. It may be pointed out that the computed values of Khan (1964) showed deviations near critical temperature from neutron diffraction data both in the case of structure factor and in the corresponding RDF. This he pointed out may be due to inherent experimental errors in the measured intensities especially near the critical temperature range.

Hence it is felt important to see how the MSM approximation works with this fluid near the critical temperature. The present potential function used is different from those of Khan. The temperature chosen is 210°K and the density is 0.75×10^{-2} atom/Å^3.

2. Theory

As is well-known the Fourier transform of the DCF is given by

$$\tilde{c}(k) = \frac{4\pi}{k}\int_0^\infty c(r) r \sin kr \, dr, \qquad \ldots (3)$$

$$c_{total}(r) = c_{hs}(r)+c_{sw}(r), \qquad \ldots (4)$$

where $c_{hs}(r)$ is the hard-sphere part and the $c_{sw}(r)$ is the square-well part of the DCF. It may be pointed out that Woodhead *et al* (1968) in their so called random phase approximation also write their $c(r)$ as a sum of $c_{hc}(r)$ and $c_{lr}(r)$ where *hc* and *lr* represent hard core and long range parts respectively. They use Wertheim's (1963) hard sphere expression for $c_{hc}(r)$ and Lennard-Jones 6–12 potential for $c_{lr}(r)$ in evaluating the structure factor of liquid argon. Hence, we further write

$$c(r) = c(r)_{Wertheim} \quad , r < \sigma \qquad \ldots (5)$$

$$c(r) = c(r)_{MSM} \quad , \sigma < r < \lambda\sigma \qquad \ldots (6)$$

and

$$c(r) = 0 \quad , r > \lambda\sigma \qquad \ldots (7)$$

The Wertheim (1963) expression for the DCF in the range $r < \sigma$ is given by

$$c(r) = -\frac{1}{(1-\eta)^4}\left[(1+2\eta)^2-6\eta(1+\eta/2)^2\left(\frac{r}{\sigma}\right)+\frac{\eta}{2}(1+2\eta)^2\left(\frac{r}{\sigma}\right)^3\right] r<\sigma \qquad (8)$$

$$\eta = \frac{\pi\rho\sigma^3}{6}, \qquad \ldots (9)$$

where $\rho = N/V$.

The square-well potential can be written as

$$u(r) = \begin{cases} \infty & , r < \sigma \\ -\epsilon & , \sigma < r < \lambda\sigma \\ 0 & , r < \lambda\sigma. \end{cases} \quad \ldots (10)$$

Hence from eq. (2) we have

$$c_{sw}(r) = \epsilon/k_B T, \qquad \sigma < r < \lambda\sigma, \quad \ldots (11)$$

Combining eqs. (8) and (11) and substituting in eq. (3) and carrying out integration gives

$$\begin{aligned} \tilde{c}_{total}(k) &= \tilde{c}_{hs}(k) + \tilde{c}_{sw}(k) \\ &= -\frac{4\pi}{k(1-\eta)^4}\left\{(1+2\eta)^2\left[\frac{1}{k^2}\sin k\sigma - \frac{\sigma}{k}\cos k\sigma\right] - \frac{6\eta}{\sigma}(1+\eta/2)^2\right. \\ &\times\left[-\frac{\sigma^2}{k}\cos k\sigma + \frac{2\sigma}{k^2}\sin k\sigma + \frac{2}{k^3}\cos k\sigma - \frac{2}{k^3}\right] + \frac{\eta}{2\sigma^3}(1+2\eta)^2\Big] \\ &\times\left[-\frac{\sigma^4}{k}\cos k\sigma + \frac{4\sigma^3}{k^2}\sin k\sigma + \frac{12\sigma^2}{k^3}\cos k\sigma - \frac{24\sigma}{k^4}\sin k\sigma - \right. \\ &\left.\left. - \frac{24}{k^5}\cos k\sigma + \frac{24}{k^5}\right]\right\} + \frac{4\pi\epsilon}{k_B T}\left\{\frac{1}{k^3}\sin\lambda k\sigma - \frac{\lambda\sigma}{k^2}\cos\lambda k\sigma - \right. \\ &\left. - \frac{1}{k^3}\sin k\sigma + \frac{\sigma}{k^2}\cos k\sigma\right\}. \quad \ldots (12) \end{aligned}$$

Eq. (12) is important since the structure factor can now be computed from the well known relation (Tago 1973)

$$S(k) = \frac{1}{1-\rho\tilde{c}(k)}, \quad \ldots (13)$$

when once the structure factor is known the RDF is evaluated from the equation

$$g(r) = \frac{1}{2\pi^2\rho_0}\int_0^\infty dk\, k^2 \frac{\sin kr}{kr}[S(k)-1]. \quad \ldots (14)$$

3. Results and Discussion

The potential parameters for krypton have been obtained by fitting the first maximum of the structure factor with the aid of eqs. (12) and (13). At this juncture it may be pointed out that in the case of Rb, Aschroft & Leckner (1966) also obtained their parameter η by fitting $S(k)$ to give correct height $S(k)_{max}$. One can also fit the parameters with the known compressibility value at $S(0)$.

However, we found it convenient to use the peak value to obtain the potential parameters.

The structure factors were calculated upto $k = 20\text{Å}^{-1}$ long before which it becomes equal to unity thus eliminating the truncation problem of the upper limit (Mikolaj & Pings 1967).

The parameters so obtained by fitting the first peak for the square-well are

$$\sigma = 3.5\text{Å}$$
$$\lambda = 1.4$$
$$\epsilon/k = 134.5°\text{K}.$$

The potential parameter used by Khan for L–J (6–12) potential function are

$$\sigma = 3.591\text{Å}$$
$$\epsilon/k = 172.7°\text{K}.$$

These values compare favourably with the present chosen values of the square-well potential. Here the computed values have been compared with experiment since the parameters of eq. (13) (and hence of eq. (12)) have been fitted with experimental maxima. However, we are also including theoretical values as evaluated by Monte Carlo (MC) techniques (Smith *et al* 1971, Watts & Henderson 1969). In this connection it may be pointed out that Aschroft & Leckner (1966) and Greenfield *et al* (1972) who used a rigid sphere potential function compared their calculated values with experiment only and the same procedure has been followed since it is clear that the present model is more realistic than those used by Aschroft and Leckner. The computed structure factor and the corresponding radial distribution function are shown in figures 1 and 2 respectively.

The present calculated structure factor values closely follow those of Khan's values obtained from the PY equation using L–J (6–12) potential (Khan 1964). In fact the agreement between the present calculated values and those of Khan are good from $k = 0.6\text{Å}^{-1}$ onwards. In the Monte Carlo (MC) or molecular dynamics (MD) method the potential parameters directly enter into the evaluation of $g(r)$ while in the present case the $g(r)$ has been obtained by numerical Fourier transform of $S(k)$ (March 1968). The corresponding RDF curve also agrees fairly well with Khan's value even though the present calculations give a lesser peak height than that obtained by Khan from PY integral equation using L–J (6–12) potential. In Khan's computations however there are deviations of $g(r)$ at large values of r while it is not so with the present model. However, in both the cases the peak height is much too smaller than the experimentally reported value of Clayton & Heaton (1961). By examining in a detailed manner and using computed values of k beyond $k = 1.38\text{Å}$, Khan was able to obtain some sort of an agreement of $g(r)$ at the first peak only. He finally concluded

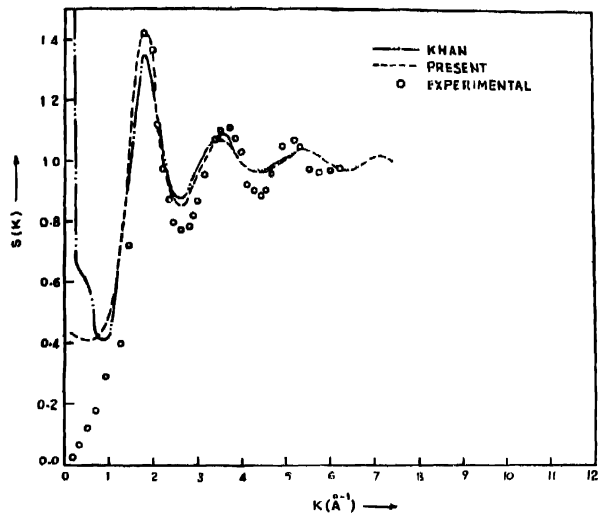

Fig. 1. Structure factor, $S(k)$, curve vs. k (Å^{-1}) for liquid krypton at $T = 210$°K and $\rho = 0.75 \times 10^{-2}$ atom/Å^3.

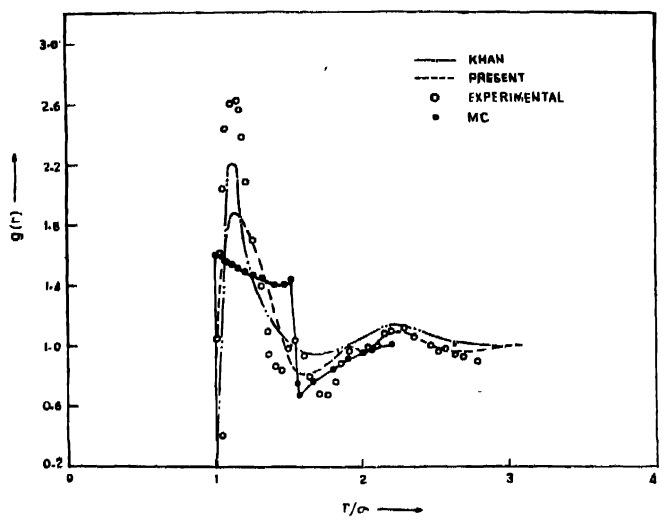

Fig. 2. Radial distribution function, $g(r)$ vs r/σ for liquid krypton at $T = 210$°K and $\rho = 0.75 \times 10^{-2}$ atom/Å^3.

that the experimental distribution curve near the critical temperature (110°K) gives too high a first peak and suggested that this computed curve is more reliable than the experimental curve. The present investigations completely support the view that experimental values of $g(r)$ near the critical temperature may be in error and the very good agreement between the $S(k)$ values obtained from

various potential functions clearly confirm this view and hence the calculated $g(r)$ may be treated as more reliable. Similar conclusions have been arrived at in the case of xenon (Khan & Broyles 1965).

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